

The accuracy of X-ray diffraction methods for determining mineral mixtures

COVADONGA BRIME

Departamento de Cristalografía y Mineralogía, Facultad de Geología, Universidad de Oviedo, Oviedo, Spain

ABSTRACT. An X-ray diffraction method has been successfully applied to the quantitative determination of mineral mixtures. The absorptive properties of the samples and the number of components determine the analytical procedure to be used. The methods described (external standard plus empirical determination of the mass attenuation coefficient) provides an accurate and rapid alternative to the direct measurement of the mass attenuation, Compton diffusion or internal standard methods. The relative accuracy obtained is of the order of 10% at the 0.1% level, independent of the sample composition.

KEYWORDS: X-ray diffraction, mineral mixtures, mass attenuation coefficient.

DETERMINATION of the quantity of a particular mineral present in a rock by X-ray diffraction methods involves the measurement of the intensity of X-ray peaks for that mineral and comparison with calibration standards. Correlation of the peak intensities with mineral concentration depends on the extent to which the reproducibility can be controlled by instrumental and specimen preparation techniques (Brime, 1978).

In order to test whether a relation exists between the actual quantity of a mineral on the sample mount and the quantitative results of the X-ray diffraction analysis, a study of three different methods for the conversion of intensities into concentration was carried out. None of the methods studied involve the mixture of the unknown sample with an internal standard.

Mineral percentage calculation. Selection of the analytical procedure

The expression for the intensity of a reflection in a powder diffraction pattern is well established and described elsewhere (Cullity, 1956; Azaroff, 1968). Alexander and Klug (1948) showed that the X-ray intensity (I_p) from the p component can be related to the weight fraction of the component (c_p) by the equation:

$$I_p = K_p \frac{c_p}{\bar{\mu}^*} \quad (1)$$

where K_p is a constant which depends upon the nature of component p and the geometry of the apparatus employed, and $\bar{\mu}^*$ is the average mass attenuation coefficient of the sample (component p included), which may be expressed as a function of the coefficients of the problem component and the matrix (m):

$$\bar{\mu}^* = c_p \mu_p^* + \mu_m^*(1 - c_p) = c_p(\mu_p^* - \mu_m^*) + \mu_m^*$$

The expression (1) becomes:

$$I_p = K_p \frac{c_p}{c_p(\mu_p^* - \mu_m^*) + \mu_m^*} \quad (2)$$

The intensity of the pure component p is:

$$I_{0p} = K_p \frac{1}{\mu_p^*}$$

combining both equations

$$I_N = \frac{I_p}{I_{0p}} = \frac{c_p}{c_p(1 - \alpha) + \alpha} \quad (3)$$

Equation (3) was first derived by Alexander and Klug (1948), where $\alpha = \mu_m^*/\mu_p^*$, and is represented in fig. 1 for different values of α .

Materials

The attenuation properties of the sample and the number of components present determine the analytical procedure to be used.

A number of samples was selected covering a range of cinnabar content, and their mineralogical composition was determined by means of X-ray diffraction using Ni-filtered Cu-K α radiation. The scan was made between $2\theta = 7^\circ$ and 62° corresponding to values of d between 12.6 and 1.496 Å.

The main component of the samples is quartz (50%). The iron sulphides, pyrite and marcasite, appear in different amounts with some iron oxide (hematite) in most of the samples, together with gypsum, anhydrite, siderite, and ankerite. The clay fraction, formed by illite and kaolinite, is easily identified in oriented aggregates.

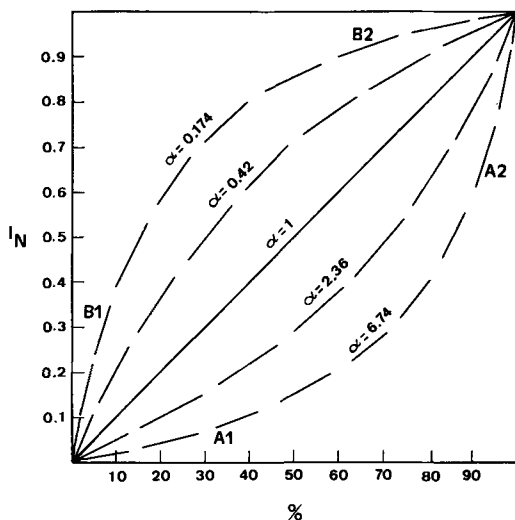


FIG. 1. Variation of a substance intensity as function of its concentration on matrices with different mass attenuation coefficients.

Cinnabar has the highest mass attenuation coefficient of the minerals present in the samples, followed by the iron minerals (Table I). The presence of iron minerals will have a great influence in the value of the mass attenuation coefficient of the matrix (formed mainly by quartz with low attenuation coefficient) and, because of this, in the intensity of the cinnabar peak.

Sensitivity of detection

In the detection of a mineral, the sensitivity depends on the mass attenuation coefficient of the other components of the mixture (equation 2).

The relationship between intensity and concentration is linear only when $\mu_p^* = \mu_m^*$. In all other cases there is a set of curves (fig. 1) that enables the following conclusions about the sensitivity of the detection and the precision of the determinations to be drawn.

If $\alpha > 1$ (zone A, fig. 1) it is possible to detect relatively large amounts of material (fig. 2). The precision of the determinations is then relatively poor for small amounts and it will be better as the concentration increases.

If $\alpha < 1$ (zone B, fig. 1) it is possible to detect small quantities of material (fig. 2). The precision of the analysis is good for small amounts of the problem substance and decreases as the concentration of the problem substance increases.

In the studied samples, as the mass attenuation coefficient of the cinnabar is larger than the co-

efficient of the other minerals present (α will always be < 1), the precision of the analysis will be high for small amounts of cinnabar.

Table I.

Calculated mass attenuation coefficient (in $\text{cm}^2 \text{g}^{-1}$) of the sample components for $\text{CuK}\alpha$ radiation.

Mineral	Mass attenuation coefficient $\text{CuK}\alpha$
Quartz	34.58
Cinnabar	198.23
Pyrite	191.98
Calcite	70.87
Ankerite	73.87
Siderite	153.70
Kaolinite	30.80
Illite	43.55-50.90
Chlorite	29.40-121.73
Gypsum	60.73
Anhydrite	74.08

Analytical peak

For the correct use of a peak in a quantitative analysis by X-ray diffraction, it is advisable to choose a peak of high intensity of the substance to be analysed, as a higher number of counts will have a minor statistical error.

Cinnabar has two peaks of high intensity, at 3.35 Å and 2.865 Å, but the first could not be used because it interferes with the main quartz peak.

Selection of the analytical method

The accuracy of the analytical results depends mainly on the application of a good system for the conversion of intensities into concentration of the components.

The 'direct comparison' method (Cullity, 1956) can only be used for a very restricted number of substances as it is unusual for the problem substance and the matrix to have the same mass attenuation coefficient. This method cannot be used here as the mass attenuation coefficient of cinnabar is 198.27 while the coefficient of the matrix ranges from 60 to 120.

The method of 'known addition (spiking)' (Gordon and Nagelschmidt, 1954; Copeland and Bragg, 1958; Cubitt, 1975) involves the inconvenience of mixing the sample. Besides this, it is essential to add material of identical characteristics to the problem substance; this is especially important considering the influence on the X-ray

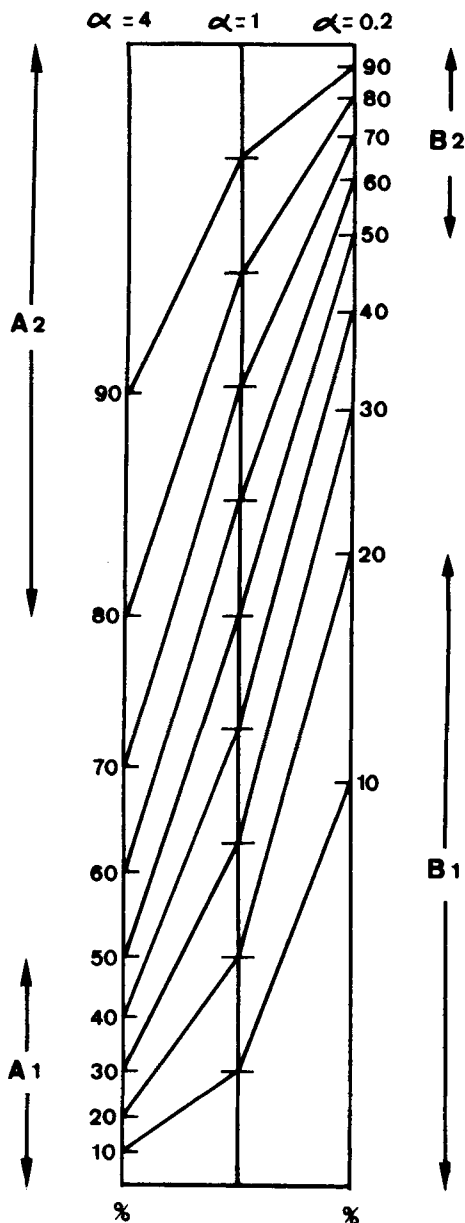


FIG. 2. Variations in peak height for a given substance as a function of different mass attenuation coefficients of the matrix: A1 Small amounts of mineral, abundant matrix. Large changes in concentration lead to small changes in peak height. A2 Large amounts of mineral in a small amount of matrix. Small variations in concentration lead to large changes in peak height. B1 Abundant matrix with small amounts of mineral. A small change in concentration will produce a large change in intensity. B2 Large amounts of mineral in a small amount of matrix. Large changes in concentration only produce small changes in intensity.

intensity of the grain size and crystallinity of the particles. Another limitation lies in the fact that the mass attenuation coefficient of the sample must be the same before and after the addition, which is very difficult to achieve due to the high mass attenuation coefficient of cinnabar.

The 'internal standard' method (Clark and Reynolds, 1936) makes it possible to eliminate the matrix effect, as the internal standard peak and the analysis peak should be attenuated by the same amount and the factor $\bar{\mu}^*$ disappears from equation (1). With this method it is possible to obtain high precision and accuracy, but it is time consuming (weighing the sample and standard, homogenizations of the samples, etc.). The main difficulty with this method appears with samples with three or four main components and several minor components as it will be very difficult to find an internal standard whose peaks do not interfere with those already present in the sample.

The 'matrix flushing' method (Chung, 1974), very similar to the internal standard method, has the advantage of not requiring a calibration curve, as all the matrix factors are flushed out of the intensity concentration equation:

$$X_i = \frac{X_f}{k_i} \left(\frac{I_i}{I_f} \right) \quad (4)$$

X_i is the weight fraction of the component i , X_f the weight fraction of flushing agent, k_i the Reference Intensity Ratio of substance i , I_i the intensity of X-rays diffracted by a selected plane (hkl) of component i , and I_f the intensity of X-rays diffracted by a selected plane (hkl) of the flushing agent. However, although it is accurate and easy to apply, the matrix flushing method involves mixing the sample with a flushing agent, so it has the same basic problems as the internal standard method.

The problem of preparation of the samples, together with the dilution caused by the addition of an internal standard or a flushing agent, is very important if the samples contain a low amount of the problem substance. The 'external standard' method and the 'Compton diffusion' method were therefore used in this study.

The 'external standard' method (Alexander and Klug, 1948; Engelhard, 1955) has the advantage of not requiring handling of the samples. It is possible to use the calibration curves obtained from equation (3) and represented in fig. 1, which allow very good results to be obtained with binary mixtures (Brime and Sancho, 1977) although the accuracy decreased slightly for a larger number of components.

The 'Compton diffusion' method (Sahores, 1969) has the simplicity of the 'external standard' method and the accuracy of the 'internal standard'. For its

use it is necessary to have a second detection channel in the diffractometer for the incoherent beam, equipment not available at Oviedo. For this reason the study of the samples was carried out at the research Laboratory of the Société National Elf-Aquitaine in Pau (France).

External standard. This method, based on the equation (3), allows the use of the curves of fig. 1 for the conversion of the intensity into percentage of the problem substance, once the value of the normalized intensity I_N is known. To determine I_N , a sample (external standard), which can be either the pure problem substance or a known sample similar to the problem substances, is used.

In the samples studied, whose mineralogical composition was given above, the percentage of the different components was not known, so we could not initially calculate either the value of the matrix mass attenuation coefficient or the value of α .

The samples, once mounted in the sample holder, were studied in the diffractometer using Ni-filtered Cu radiation, and their intensity was measured with runs at constant angular velocity ($\frac{1}{2}^\circ/\text{min.}$).

To obtain the percentage of cinnabar in each sample it is possible to: (a) Use as external standard a sample of similar characteristics to the average problem sample but whose cinnabar content is known. Assuming that the matrix is formed only by quartz, the cinnabar content can be determined from the curve corresponding to a value of $\alpha = \mu_{\text{SiO}_2}^* / \mu_{\text{HgS}}^* = 0.174$. As the standard is not the pure problem sample, the normalized intensity cannot be determined directly by the simple ratio of the intensities of the problem sample and the standard. It is necessary to have previously calculated a factor F ($F = (I_N)_{\text{standard}} / (I_p)_{\text{standard}}$) which allows the conversion of the intensity measured with the apparatus (I_p) into normalized intensity (I_N) (Table II, col. 1). This factor F is also used to correct the matrix effect, as the intensity of the standard sample and the problem samples will be attenuated by a similar amount. In this way the values shown in Table II, col. 2, were obtained. (b) Alternatively, an external standard containing only the problem substance can be used. In this case the intensity is not corrected for the matrix effect

Table II.

Cinnabar % determined from the curve of $\alpha = 0.174$ using as external standard a sample similar to the problem samples.

Sample	1	2	3
53	0.020	0.35	51.5
63	0.105	1.99	110.6
64	0.273	6.15	145.0
71	0.040	0.72	72.0
74	0.066	1.21	91.0
75	0.079	1.48	100.0
76	0.080	1.47	100.7
80	0.011	0.18	33.6
81	0.030	0.54	63.6
83	0.090	1.58	78.4
86	0.551	17.60	212.5
89	0.027	0.48	61.2
106	0.027	0.48	54.2
107	0.023	0.40	50.6
113	0.211	4.46	128.8
116	0.084	1.57	79.3
121	0.146	2.79	89.7
126	0.580	19.38	238.1

1. Normalized intensity $I_N = I_p \times F$

2. % HgS

3. Accuracy index of the X-ray determinations of col. 2.

Table III. Cinnabar % determined using as external standard a sample of pure cinnabar.

Sample	1	2	3	4	5	6
53	$9.60 \cdot 10^{-3}$	84	0.17	24.8	0.40	60.0
63	0.050	68	0.90	50.0	1.76	97.6
64	0.131	73	2.54	59.9	5.28	124.6
71	0.019	95	0.33	33.0	0.92	92.0
74	0.031	96	0.54	40.6	1.53	115.0
75	0.038	73	0.66	44.6	1.40	94.6
76	0.038	73	0.66	45.2	1.40	94.6
80	$5.04 \cdot 10^{-3}$	107	0.08	16.0	0.27	50.0
81	0.015	82	0.26	30.6	0.62	73.0
83	0.043	99	0.76	37.6	2.20	111.1
86	0.264	60	5.86	70.8	9.71	117.3
89	0.013	82	0.22	28.2	0.54	69.0
106	0.013	120	0.22	24.7	0.78	88.0
107	0.011	120	0.19	24.1	0.66	84.0
113	0.101	63	1.90	54.9	3.47	100.3
116	0.040	99	0.71	35.9	2.04	103.1
121	0.070	80	1.28	39.7	2.99	92.8
126	0.278	60	6.26	76.9	10.35	127.2

1. Normalized intensity $I_N = I_p / I_{Op}$

2. Mass attenuation coefficient of matrix μ_m^*

3. % HgS obtained from the curve corresponding to a value of $\alpha = 0.174$

4. Accuracy index of the % HgS of col. 3

5. % HgS obtained from the curves corresponding to $\alpha = \mu_m^* / \mu_{\text{HgS}}^*$

6. Accuracy index of the % HgS of col. 5

and it is therefore not advisable to use the curve $\alpha = 0.174$, because as the samples contain iron oxides and sulphides and carbonates with a high mass attenuation coefficient (Table I), the mass attenuation coefficient of the matrix is larger than 34.58 (mass attenuation coefficient of quartz). If, in spite of this, the curve corresponding to a value of $\alpha = 0.174$ is used, the results will have a high negative bias (Table III, col. 3).

It is thus necessary to know the mass attenuation coefficient of the matrix to determine the value of α and hence the percentage of cinnabar in the samples. To determine this coefficient, a procedure based on the method described by Ferrero (1966) for sedimentary rocks was followed. An important fraction of the samples is formed by clay minerals, which are difficult to quantify on powder diagrams, due to the low intensity of their peaks, and due also to the difficulty of calculating their mass

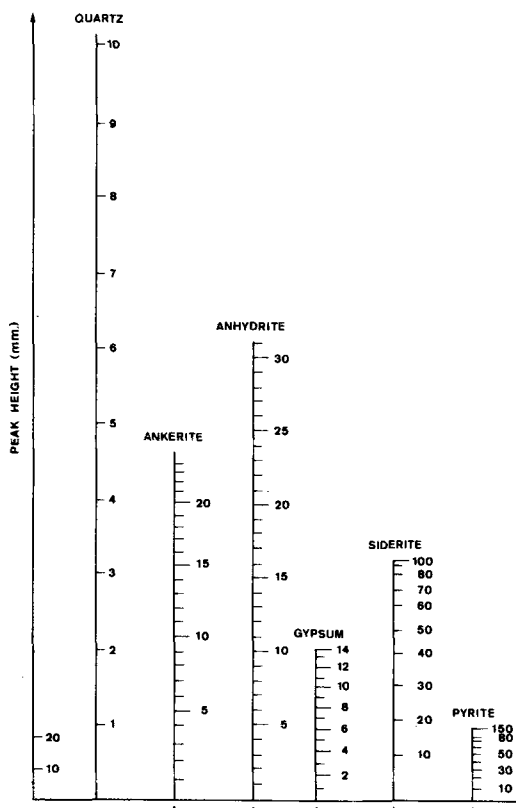


FIG. 3. Diagram used for the determination of the matrix mass attenuation coefficient (after Ferrero, 1966). Facing the minerals peak height are corresponding modifications of the initial coefficient. The sum of these modifications and the initial coefficient will give the mass attenuation coefficient of the matrix.

attenuation coefficient, as the composition of these minerals may change. For this reason an arbitrary value of 47, close to the average of their mass attenuation coefficients (Table I), was chosen. This initial value was later modified following measurement of the intensity diffracted by the different components in the samples (fig. 3). Table III, col. 2, shows the values of the mass attenuation coefficient of the problem samples obtained in this way, from which it was possible to determine values of α and, eventually, the cinnabar content of the samples (Table III, col. 5).

Both methods have identical precision as they have been derived from the same intensity values. Thus, the differences observed in the results are due only to the kind of method used in the conversion of the intensities into cinnabar %.

In order to assess the degree of accuracy obtained by means of X-ray diffraction determinations, the cinnabar content of the samples was determined by suitable chemical methods, and the values obtained were taken as reference to calculate the accuracy index of the X-ray determinations ($AI = 100 \times \%HgS_D / \%HgS_R$).

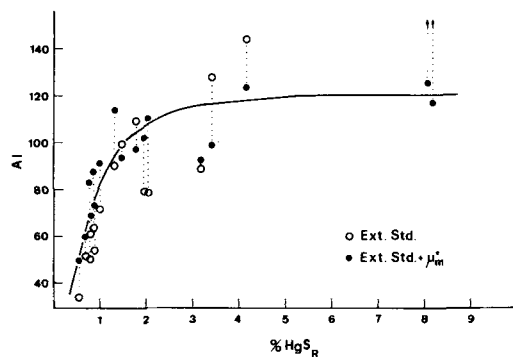


FIG. 4. Relation between accuracy index (AI) of the determinations done using the external standard method and the reference cinnabar content of the samples. \circ External standard a sample of similar characteristics to the problem samples. \bullet External standard of pure cinnabar plus correction of the mass attenuation coefficient of the matrix.

In fig. 4 the accuracy index (AI) of the determinations versus the reference cinnabar content of the samples is plotted. The more accurate results are obtained for % ranging from 1 to 2%.

In fig. 5 the regression lines relating the data obtained with each diffraction method to the % used as reference are plotted. The lines cross at a point, corresponding to a % of 1.5. While the values obtained by method (b) correspond quite well with

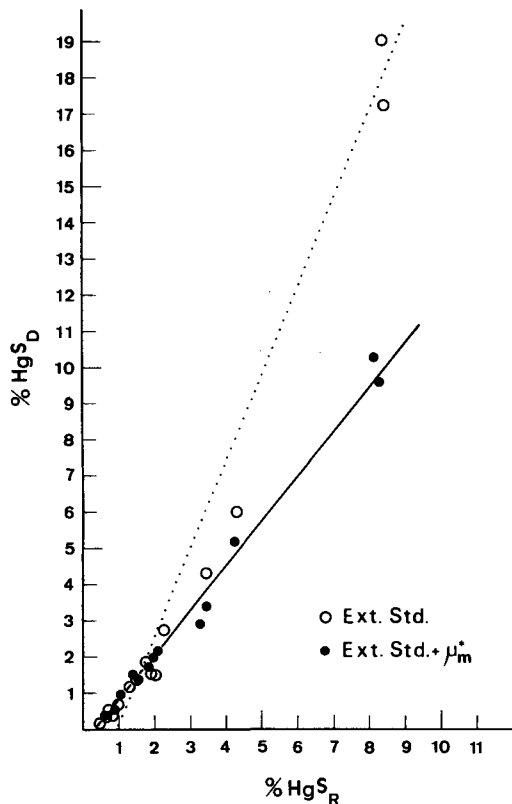


FIG. 5. Cinnabar content determined by X-ray diffraction, external standard method, ($\% \text{HgS}_D$) versus the reference content ($\% \text{HgS}_R$). Symbols as in fig. 4.

the reference values it is not true for the values obtained by method (a).

The correlation indices are 0.996 and 0.978 respectively which show that with the second of the methods described above, the values obtained are more accurate. This can be explained because in the latter case the correction corresponding to each sample matrix composition was applied, while in the former, as the same correction was applied to all the samples, the results will be exact only if the samples have no variation in respect to the standard sample. Any variation will impart a bias to the results obtained—an excess if its coefficient is smaller than that of the standard sample, or a deficiency if the contrary occurs.

If these results are compared with those obtained for binary mixtures (Brime and Sancho, 1977) it is seen that the accuracy changes with the number of components of the problem sample, with a correlation coefficient of 0.999 for binary mixtures and 0.996 for samples with several components.

Compton diffusion. This method (Sahores, 1969) makes it possible to determine the cinnabar content of the samples if the values of the coherent and incoherent intensities are known. Following Sahores (1969), the Compton intensity for constant experimental conditions is given by:

$$I_C = \frac{K_\alpha}{\bar{\mu}^*} \quad (5)$$

The ratio I_p/I_C is therefore independent of $\bar{\mu}^*$ and it is a linear function of c_p since the corresponding calibration curve is a straight line.

To determine the calibration curve for the cinnabar, all that is needed is a set of samples with known contents of cinnabar in which both intensities have been measured (Table IV). From these values, and using a simple program of linear regression, the following equation was obtained:

$$\% \text{HgS} = 0.36 + 3.37(I_p/I_C) \quad (6)$$

This equation represents the calibration line for cinnabar used in the present work to determine its percentage in the problem samples.

Table IV.
Intensity ratio and cinnabar content in the standard samples.

Sample	1	2
1	0.26	1.20
2	0.66	2.54
3	1.49	5.35
4	3.40	11.82
5	6.91	23.70

1. Ratio I_p / I_C
2. % HgS

After the measurement of the Compton intensities of the samples, the ratio I_p/I_C was obtained (Table V, col. 1) and by means of the equation (6) the cinnabar content of the samples determined (Table V, col. 2).

If the accuracy index (Table V, col. 3) is plotted against the cinnabar % (fig. 6), it can be seen that it changes with the concentration, reaching an optimum value for cinnabar contents between 1.5 and 2%.

The correlation between the experimental results and the reference chemical values (fig. 7) is very good ($r = 0.999$) for all the samples and is independent of their mass attenuation coefficients.

Table V.
Cinnabar content of the samples determined by the Compton diffusion method.

Sample	1	2	3
53	0.07	0.63	92.3
63	0.42	1.79	99.4
64	1.14	4.21	99.3
71	1.72	0.94	94.0
74	0.28	1.32	99.3
75	0.33	1.47	99.3
76	0.32	1.45	99.3
80	0.04	0.51	92.7
81	0.15	0.80	94.1
83	0.48	0.51	92.7
86	2.31	8.17	98.7
89	0.11	0.73	93.6
106	0.14	0.84	94.4
107	0.11	0.74	93.7
113	0.91	3.43	99.1
116	0.47	1.96	98.9
121	0.84	3.20	99.4
126	2.27	8.03	98.6

1. Ratio I_p / I_C

2. % HgS_C

3. Accuracy index of the % HgS of col. 2

Conclusions

After the comparative study of the quantitative methods used, it is concluded that: (a) Analyses made using as external standard a sample similar to the problem ones, are quicker and easier, but also are less accurate. (b) The accuracies obtained by the different methods (Tables II, III, and V), show that the Compton diffusion method yields the best results. (c) If the pure problem substance is used as an external standard and the mass attenuation coefficient is determined empirically, we gain the advantages of the two methods because, although the accuracy is slightly lower than that obtained with the Compton method, it does not require any kind of additional equipment. On the other hand, the possible extra time required for the determination of the mass attenuation coefficient in the external standard method is balanced by the higher accuracy obtained. (d) The three methods yield the best accuracy for cinnabar concentrations ranging between 1 and 2% (figs. 4 and 6), the interval belonging to the zone called B1 (figs. 1 and 2) in which small concentration variations produce con-

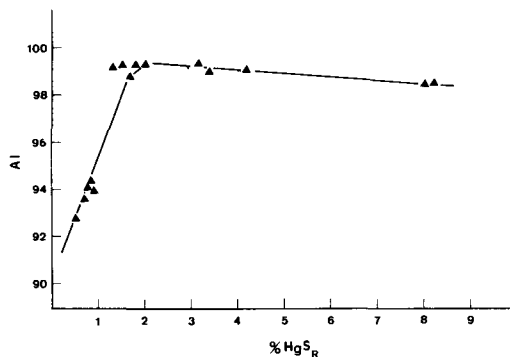


FIG. 6. Variation of the accuracy index (AI), of the samples determined by the Compton method, for changing cinnabar content.

siderable changes in intensity. (e) The sensitivity of the detection depends on the mass attenuation coefficient of the samples and varies between 0.6 and 0.8% of cinnabar. (f) The external standard method has the advantage of not requiring any manipulation of the samples, and it is possible to use the theoretical curves obtained from equation (3) and plotted in fig. 1. In this way very good results were obtained with binary samples (relative accuracy of 5% at the 0.05% level, Brime and Sancho, 1977), although the accuracy diminishes as the number of components increases. Because of this the external standard method has been combined with the empirical determination of the

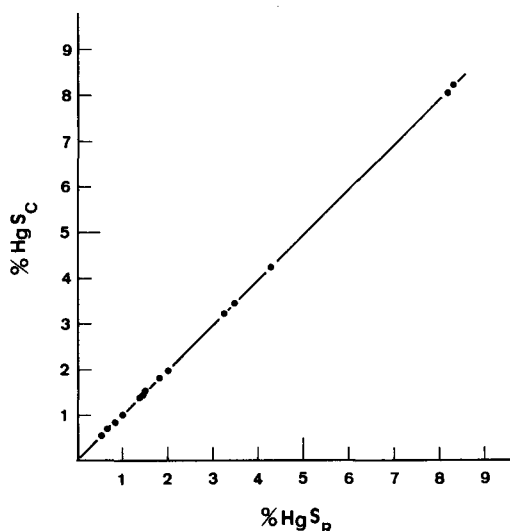


FIG. 7. Cinnabar content determined by the Compton method (% HgS_C) versus the reference content (% HgS_R).

matrix attenuation coefficient using the diagram plotted in fig. 3, giving values with a relative accuracy of 10% at the 0.1% level. (g) For the application of the Compton method a calibration curve (equation 6) was established from a set of samples with known composition giving results with a relative accuracy of 5% at the 0.05% level.

From the above, it can be concluded that X-ray diffraction is a suitable method for routine quantitative analysis because it is quick and non-destructive; the analytical equipment required has many applications and can be applied to any kind of sample.

Finally, the method here described (external standard plus empirical determination of the mass attenuation coefficient) provides an accurate and rapid alternative to the direct measurement of the mass attenuation, Compton diffusion, or to the internal standard methods, having besides the above mentioned the following characteristics: easy sample preparation; quick and simple conversion of intensities into mineral percentages; relative accuracy of 10% at the 0.1% level; independence from the sample composition; shorter time required for the analysis is at least 30% less than the time required for the same analysis by chemical analysis.

Acknowledgements. The author wishes to record her thanks to F. Alvarez for his continuous help and encouragement and to Dr R. M. F. Preston and the

unnamed referee who critically reviewed earlier drafts of this paper.

REFERENCES

- Alexander, L. E., and Klug, H. P. (1948) *Anal. Chem.* **20**, 886-9.
- Azaroff, L. V. (1968) *Elements of X-ray Crystallography*, McGraw-Hill Book Co., New York, 610 pp.
- Brime, C. (1978) Unpub. Ph.D. thesis. Universidad de Oviedo, 153 pp.
- and Sancho, J. P. (1977) *Industria Minera*, **173**, 43-9.
- Chung, F. H. (1974) *J. Appl. Crystallogr.* **7**, 526-31.
- Clark, G. L., and Reynolds, D. H. (1936) *Ind. Eng. Chem. (Anal.)* **8**, 36-40.
- Copeland, L. E., and Bragg, R. H. (1958) *Anal. Chem.* **30**, 196-201.
- Cubitt, J. M. (1975) *J. Sediment. Petrol.* **45**, 546-53.
- Cullity, B. D. (1956) *Elements of X-ray diffraction*. Addison and Wesley Publ. Co., USA, 514 pp.
- Engelhardt, W. (1955) *Z. Kristallogr.* **106**, 430-59.
- Ferrero, J. (1966) *Nouvelle méthode empirique pour le dosage des minéraux par diffraction de R.X.* Rapp. C.F.P. (Unpubl.).
- Gordon, R. L., and Nagelschmidt, G. (1954) *Acta Crystallogr.* **7**, 626-35.
- Sahores, J. J. (1969) *Emploi du rayonnement diffusé Compton en diffractométrie X comme correcteur des erreurs dues à l'absorption*. 30^{ème} Congrès du G.A.M.S., Paris, 15 pp.

[Manuscript received 14 May 1984;
revised 1 October 1984]